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Excited state absorption of the $\text{Cr}^{6+}\text{O}^{2-}$ center in $\text{Li}_2\text{B}_4\text{O}_7$ glass

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ABSTRACT

We present excited state absorption (ESA) measurements of the $\text{Cr}:\text{Li}_2\text{B}_4\text{O}_7$ glass ($\text{Cr}:\text{LBO}$ -glass) along with preliminary interpretation. The most distinct feature in the ESA characteristics is connected with the presence of chromium in its hexa- (d^0) valence states. The Cr^{6+} ions appear to contribute in the deexcitation processes and their evidence can be seen in the ESA spectra under excitation wavelength at 308 nm. We interpret the ESA spectra detected with UV excitation in terms of transitions in the framework of Cr^{5+}O^- center which forms after charge- transfer -type absorption in $[\text{CrO}_4]^{2-}$ group. We assume the presence of the double-electron state of the $3d^22p^4$ electronic configuration together with crystal field-split states of the $3d^12p^5$ configuration, both allow to reproduce the obtained ESA spectra.

Keywords: absorption (ESA), $\text{Cr}:\text{Li}_2\text{B}_4\text{O}_7$ glass

1. INTRODUCTION

Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) is a well known material, which found numerous optoelectronic applications¹⁻³ but so far it has not yet been used as a primary laser host or gain medium. This is because of the tight packing of LBO single crystal lattice and the relatively large sizes of the dopant ions that are of interest, for example Cr^{3+} ions. In glass matrix situation is different because the glasses have more loose and relaxed structures and are more "dopant friendly" allowing much higher concentrations doping than in crystals. The optical spectroscopy of the Cr^{3+} ions in the LBO glass has been described in detail in several papers⁴⁻⁶. In this contribution, after making sure that Cr^{3+} in the LBO glass is rather poor candidate for lasing medium (because of the high strength of the ESA transitions)⁷, we focus our attention on other chromium ions: Cr^{6+} that, take important part in the deexcitation process. Their presence produces the highest distinct peak in the absorption spectrum, situated around 360 nm, hence in our investigation we used the UV excitation by the XeCl excimer laser working at 308 nm.

2. EXPERIMENTAL

The excited state absorption (ESA) spectra were measured using a setup which utilized a RD-EXC-150/25 XeCl excimer laser (308 nm) as a source of excitation, a Hamamatsu Xe flash lamp as a source of probe beam and ORIEL InstaSpec II photodiode array detector coupled to MultiSpec 1/8 m spectrograph in the detection branch. The setup operated in pulsed regime and transverse geometry⁸. The 308 nm line excites the $\text{Cr}:\text{LBO}$ glass within the highest absorption peak which can be ascribed to the following charge transfer transition in the frame of $[\text{CrO}_4]^{2-}$ group: $\text{Cr}^{6+}\text{O}^{2-} (3d^02p^6) \rightarrow \text{Cr}^{5+}\text{O}^- (3d^12p^5)$,⁹⁻¹¹

3. RESULTS AND DISCUSSION

The ESA spectrum of the $\text{Cr}:\text{LBO}$ glass sample is presented in figure 1. As it is seen, there is no chance to fit this ESA spectrum by a single Gaussian function, whereas two Gaussians {one relatively narrow (2800 cm^{-1}) and another much broader (8200 cm^{-1})} fit the spectrum perfectly. This strongly suggests that the observed ESA under UV excitation consists of transitions to two distinctly defined excited states.

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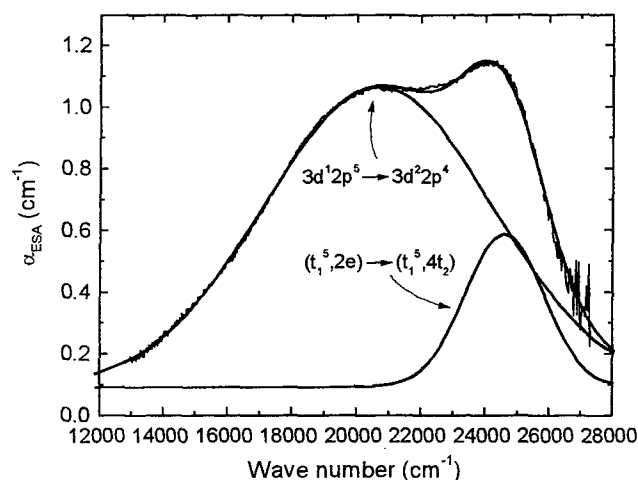


Fig. 1 Experimental ESA spectrum obtained for 308 nm excitation, fit by two Gaussians, and assignment of the contributing ESA bands.

Table I Parameters used to creation of the SCC diagram explaining the ESA spectra shown in Fig. 1. κ is the elastic constant and Γ_i are the half-widths corresponding to the respective relaxation energies

Parameter	Energy (cm ⁻¹)
κ	8000
$\eta\omega$	250
$\eta\omega'$	400
kT	200
CT_1	27933
CT_2	42500
Γ_1	4450
Γ_2	8200
Γ_3	2800
ESA_1	20520
ESA_2	24600

The single configuration coordinate (SCC) diagram can be used to reproduce a characteristic ESA spectrum comparable to that obtained with 308 nm excitation (figure 1). To achieve this, certain assumption has to be made, namely - the existence of additional excited electronic manifold, strongly coupled to the lattice, not detectable in the ground state absorption (GSA) spectrum. Such a state can be related to the $3d^2 2p^4$ electronic configuration of the central ion - ligand system. The $3d^2 2p^4$ excited electronic configuration originates from the consecutive excitation of two electrons from the valence band (made mostly of ligands orbitals) to the d orbitals of the central ion.

The resulting SCC diagram calculated using the parameters given in Table I is presented in figure 2 together with definitions of energies taken from the experiment. It shows two positions of the state $|3\rangle$ ($3d^2 2p^4$) (dashed and solid) corresponding to two qualitatively different situations described in the caption. We believe that the real situation is closer to that represented by solid line parabola of the state $|3\rangle$ ($3d^2 2p^4$) because such a positioning of the state $|3\rangle$ explains lack of emission from the higher excited state as well as other ESA bands when exciting the $Cr^{6+}O^{2-}$ center.

Considering the nature of the electronic configurations which the SCC diagram is constructed from, one should remember that $Cr^{6+}O^{2-}$ center is a typical d^0 complex (of approximated T_d symmetry). Then it is possible to write formally the electronic configuration of the central ion-ligand system as $3d^0 2p^6$.¹¹ The exemplary molecular orbital diagram for tetrahedral MX_4 complex¹²⁻¹⁴ is illustrated in figure 3. It is noted that the highest occupied bonding orbital t_1 of the ground state of such a complex is composed exclusively from ligand p_π orbitals. The higher, nonbonding molecular orbital $2e$ is of d type and consists mostly d orbital of the central ion, whereas the next antibonding orbital $4t_2$ is a typical mixed orbital consisting d orbital of the central ion but also p_σ orbitals of the ligands.

This is why the parabola corresponding to $(t_1^5, 4t_2)$ symmetry is shifted with respect to the $(t_1^5, 2e)$ parabola (different charge distributions and consequently different couplings to the lattice). The ground state absorption (CT_1) is due to one of the t_1 electrons, making a transition to the $2e$ orbital and leaving a hole in the bonds. Because the transition occurs practically from the ligands to central-ion d orbital, this is what is usually called "charge transfer transition", resulting in a distinct charge redistribution. This is consistent with the right-hand shift of the first excited state parabola. There is also another absorption, CT_2 , which is involved with a transition of one of the t_1 electrons to $4t_2$ orbital with suitably smaller charge redistribution. Thus the CT transition transforms the center $Cr^{6+}O^{2-}$ to $Cr^{5+}O^-$ center of $3d^1 2p^5$ configuration.¹¹ The larger energy ESA transition (ESA_2) is from d-type $2e$ to more diffused $4t_2$ orbital of mixed d-p type. This is also charge redistribution (simplifying: from central ion back to ligands) which results in the $(t_1^5, 4t_2)$ parabola shifted back in respect to shift of the $(t_1^5, 2e)$ parabola, almost to the same position as the ground state parabola. The smaller energy ESA transition

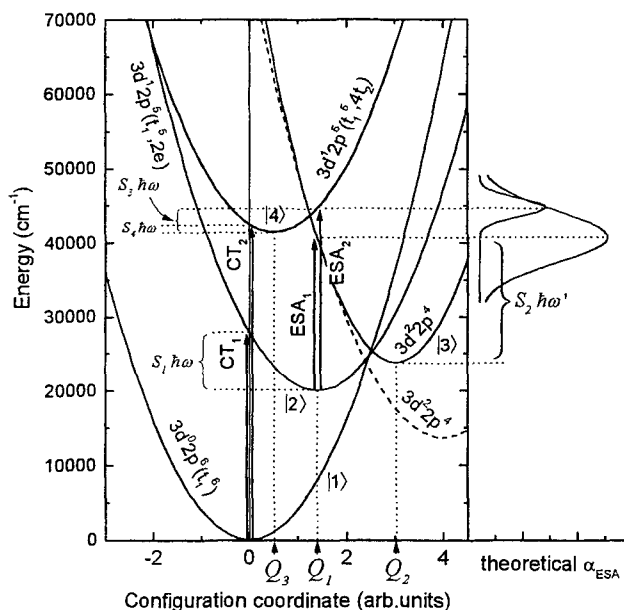


Fig. 2 SCC diagram quantitatively reproducing the ESA spectrum obtained with 308 nm excitation. Right side of the figure shows two Gaussian ESA spectra (of the widths corresponding to the respective relaxation energies) whose composition fits the experiment. The dashed parabola corresponds to the $3d^{12}p^4$ state of linear coupling to the lattice i.e. with the same phonon energy as all remaining states ($\eta\omega = 250 \text{ cm}^{-1}$). The solid parabola of the $3d^{12}p^4$ state corresponds to th different phonon energy $\eta\omega' = 400 \text{ cm}^{-1}$.

(ESA₁) occurs also from the state of $(t_1^5, 2e)$ configuration but to the state of quite different electronic configuration, namely $3d^{12}p^4$.

The model discussed above and the goodness of the fit to experimental data suggested the manifold involved of the $3d^{12}p^4$ electronic configuration.

4. CONCLUSION

In the Cr:LBO glass an important role in the deexcitation process is played by charge transfer absorption in the frame of $[\text{CrO}_4]^{2-}$ group. Excitation into the charge transfer peak, situated at 362 nm, does not lead to apparent emission but, instead, to intensive excited state absorption. The spectrum of this absorption can be fully explained in terms of the excitation of the d^0 -type complex: $[\text{CrO}_4]^{2-}$. This excitation gives rise to creation of the Cr^{5+}O^- center of $3d^{12}p^5$ electronic configuration of two terms split in the crystal field: $2e$ and $4t_2$. Transition between them is a source of shorter wavelength component of the ESA spectrum. Longer wavelength, broadband component of the ESA spectrum is caused by double-electron state of $3d^{12}p^4$ configuration ($\text{Cr}^{4+}\text{O}_2^-$ center) which forms after two consecutive transfers of the ligand electrons onto the central ion. This double-electron state plays a role of terminal ESA state.

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REFERENCES

1. R. Komatsu, T. Sugawara, K. Sassa, N. Sakura, Z. Liu, S. Izumida, Y. Segawa, S. Uda, T. Fukuda, and K. Yamanouchi, "Growth and ultraviolet application of $\text{Li}_2\text{B}_4\text{O}_7$ crystals: generation of the fourth and fifth harmonics of $\text{Nd}:\text{Y}_3\text{Al}_5\text{O}_{12}$ lasers", *Appl. Phys. Lett.* **70**, 3492-3494, 1997
2. A. Ciocan, J. Uebbing, and K. Niemax, "Analytical application of the microwave induced plasma used with laser ablation of solid samples", *Spectrochimica Acta B*, **47B**, 611-617, 1992
3. J. Gasiot, P. Braunlich, and J.P. Fillard, "Laser heating in thermoluminescence dosimetry", *J. Appl. Phys.* **53**, 5200-5209, 1982
4. F. Rasheed, K.P. O'Donnell, B. Henderson, and D.B. Hollis, "Disorder and the optical spectroscopy of Cr^{3+} -doped glasses: II. Glasses with high and low ligand fields", *J. Phys.: Condens. Matter* **3**, 3825-3840, 1991
5. B. Henderson, M. Yamaga, Y. Gao, and K.P. O'Donnell, "Disorder and nonradiative decay of Cr^{3+} -doped glasses", *Phys. Rev. B* **46**, 652-661, 1992

6. M. Yamaga, Y. Gao, K.P. O'Donnell, and B. Henderson, "Disorder and the non-radiative decay of Cr^{3+} -doped glasses", *J. Luminescence* **53**, 457-460, 1992
7. Cz. Koepke, K. Wiśniewski, M. Grinberg, A. Majchrowski, and T.P.J. Han, "Excited state absorption in chromium doped $\text{Li}_2\text{B}_4\text{O}_7$ glass", submitted to *J. Phys. Cond. Matter*
8. Cz. Koepke, A. J. Wojtowicz, and A. Lempicki, "Excited-state absorption in excimer-pumped CaWO_4 crystals", *J. Luminescence* **54**, 345-355, 1993
9. T. Murata, M. Torisaka, H. Takebe, and K. Morinaga, "Compositional dependence of the valency state of Cr ions in oxide glasses", *J. Non-Cryst. Solids* **220**, 139-146, 1997
10. M. Casalboni, V. Ciafardone, G. Giuli, B. Izzi, E. Paris, and P. Proposito, "An optical study of silicate glass containing Cr^{3+} and Cr^{6+} ions", *J. Phys.: Condens. Matter* **8**, 9059-9069, 1996
11. H. Yuan, W. Jia, D. Cohen, W. M. Yen, and B. G. Aitken, "Optical spectroscopy of pentavalent chromium ions in glass", *Mat. Res. Soc. Symp. Proc.* **455**, 483-488, 1997
12. C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory* (W.A. Benjamin, Inc.) New York, Amsterdam 1964, pp 123-128
13. M. Karplus and R. N. Porter, *Atoms and Molecules; An Introduction for Students of Physical Chemistry* (W.A. Benjamin, New York 1970)
14. B. N. Figgis, *Introduction to Ligand Fields* (Interscience, Wiley, New York 1966) pp 196-200

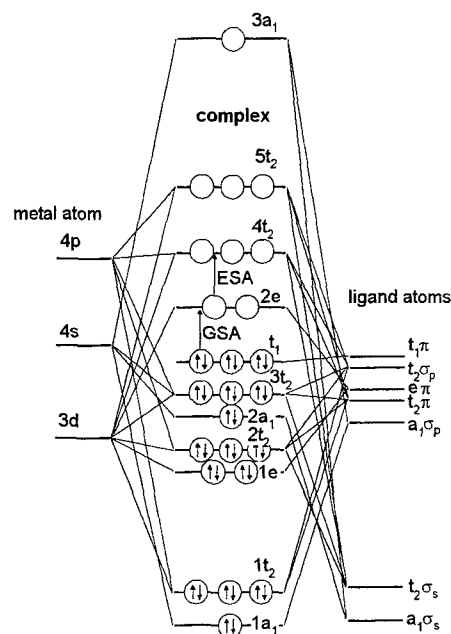


Fig. 3 Schematic molecular orbital energy level diagram for MX_4 type complexes (after Ballhausen and Gray¹¹, where the case of MnO_4^- complex was considered). The GSA and ESA transitions are indicated.